Analyzing Frequency Spectra of Dielectric Loss to Clarify Influence of L,α-alanine Doping on Phase Transition in Triglycine Sulfate

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crossref http://dx.doi.org/10.5755/j02.ms.29313

Received 22 June 2021; accepted 05 July 2021

As reported in the literature, the doping of L,α-alanine (LA) led to increasing the phase transition temperature in triglycine sulfate (TGS) – a bio-ferroelectric material that has been widely applied in industry. The nature of this anomaly is commonly investigated by considerably complicated theoretical and experimental techniques. Unlike previous studies, the present work proposes a simple physical method of analyzing frequency spectra for dielectric loss to clarify the relationship between the movement of phase transition positions and the shift of relaxation frequencies observed in the spectra. The experimental results obtained for LA-doped TGS samples synthesized at different LA contents (0, 5, 10, 20, and 30 wt.%) were used for the analysis. It was indicated that the increase in phase transition temperature was accompanied by the decrease in relaxation frequencies due to the enhanced viscosity created by strong hydrogen bonds formed between amino acids of alanine and TGS structure.
Keywords: frequency spectra of dielectric loss, L,α-alanine, glycine, triglycine sulfate, hydrogen bonds.

1. INTRODUCTION

TGS is a bio-ferroelectric material [1] with state-of-the-art applications in UV tunable laser, infrared sensors, and detectors [2, 3]. α-alanine [NH_2–$CH(CH_3)$–COOH] is known as an α-amino acid that takes part in the biosynthesis of proteins [4 – 6]. In some cases, α – alanine in general and L,α-alanine (LA) in particular can play the role of substitutional impurity in several hydrogen – bonded crystals in which triglycine sulfate (TGS) is a typical one. The presence of LA in the TGS structure helps to improve TGS characteristics satisfying strict requirements in practice. TGS consists of three groups of glycine which is isomorphic to L,α-alanine, and therefore the links between these glycine groups and L,α-alanine molecules could be easily formed through hydrogen bonds [7, 8]. Hydrogen bonds in general attract great attention from researchers because of their importance in nature [9 – 11]. Due to the presence of glycine groups in its structure, TGS has been considered as a model subject for investigating the influence of amino acids on bio-ferroelectric materials.

The crystals of L,α-alanine doped triglycine sulfate (LATGS) have been widely synthesized and reported in the literature [8, 12 – 14], so the influence of LA on properties of TGS was well studied. Regardless of the diversity of synthesis methods that can affect TGS characteristics in different ways, two general anomalies can be emphasized. Firstly, LA impurity drags the phase transition point of TGS (T_c ~ + 49 °C) toward higher temperatures. For examples, this point was determined at 49.8, 50.6, 50.9 °C [8, 15] or 49.1, 49.5, 50.9 and 51.5 °C [16] depending on growth conditions. Secondly, the higher the LA content in TGS, the higher the shift of T_c and the stronger the suppression of domain structure along *b* – the direction in relation to the disappearance of mirror symmetry [8, 17, 18].

In several studies [8, 15], the authors used spectra of dielectric constant to investigate the phase transition in LATGS. However, this method was not able to provide the exact reason, and the given explanations stopped only at assumptions. Meanwhile, the response of materials with a frequency of an external field is preferred to study dynamic characteristics of a system [19]. In materials science, frequency spectra are useful to explore the features of materials at the molecule level, and these findings can be used to explain several properties of materials. Depending on the nature of each substance, their response toward frequency occurs in different ways.

As far as we are concerned, several study methods have been utilized to explore the properties of TGS under the effects of LA doping, including dielectric measurements [8, 17], morphological techniques [17, 20], electron emission [21], and theoretical calculations [7]. However, frequency spectra of dielectric loss have not been employed yet. In this regard, the present work brings the idea that the decryption of frequency spectra may help us to predict and explain anomalous phase transition in LA doped TGS.

2. SAMPLES SYNTHESIS AND EXPERIMENTAL TECHNIQUES

The pure and LA-doped TGS crystals employed to export frequency spectra in this study were grown from TGS-water solutions by decreasing the saturation temperatures from 25 to - 5 °C with different LA concentrations of 5, 10, 20, and 30 %. The growth conditions were strictly controlled (temperature fluctuation within ± 0.05 °C, the rotation speed of 10 rpm, temperature reduction rate of solution ranged in 0.4 – 0.5 °C per day). The method of decreasing saturation temperatures to

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negative ones takes advantage of other techniques. The main reason is related to the ability to form a large number of defects in TGS originated from the intensification of interaction between polar LA and TGS lattice due to the partial contribution of polar water clusters appeared at 0 °C. From our point of view, this is useful for frequency response because polar molecule groups are sensitive to electric field reversal. In this regard, frequency spectra could make sense for analyzing the influence of LA.

For dielectric measurements, a silver paste was applied to make electrodes on the large surfaces of samples. To remove possible water, the samples have been dried at 120 °C for 2 h and then left for cooling down at room temperature. The experiments were repeated three times to confirm the reliability of the data.

Prior to testing frequency response, the samples were carefully characterized by XRD (Rigaku Ultima IV) and FTIR (Bruker Tensor 37, USA) techniques. Next, the phase transition of pure and LA doped TGS samples was also determined on a model GW Instek LCR-821 meter at 1 kHz. These characteristics obtained above are essentially important to confirm the quality of samples. The frequency spectra were taken on a system consisting of an impedance gain/phase analyzer (Solartron -1260A, UK) and a module (Dielectric Interface – 1296, UK) at different temperatures.

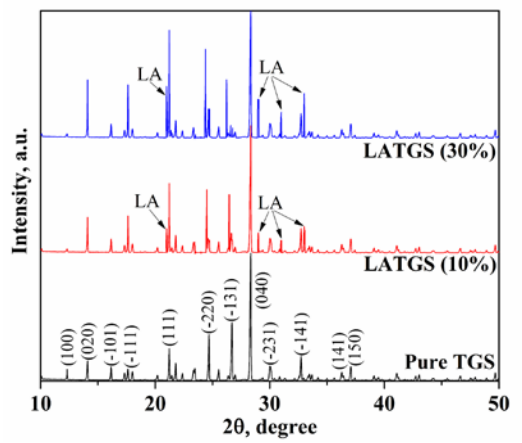
3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Reliability of the synthesized samples

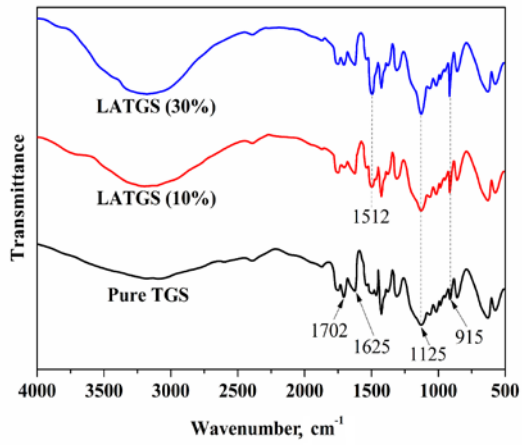
In order to confirm the quality of the synthesized samples, materials are needed to be characterized and compared with those reported in the literature. As shown in Fig. 1 a, the XRD pattern for pure TGS samples is in good agreement with ICPDS XRD data (00-015-0947) containing all characteristic peaks. Introducing LA into TGS led to increasing the intensity of several peaks of (020), (-111), (111), (-220) and (-131), confirming the results observed in previous studies as [22, 23]. In addition, the peaks at 21.1°, 29°, 31.2° and 33° typical for LA [24] were also detected (Fig.1a). Besides, the presence of LA in TGS moved the peak at 24.7°(-220) and 26.7°(-131) to the new positions of 24.5° and 26.4° (LA-Doped TGS 10 %), 24.3° and 26.2° (LA-Doped TGS 30 %), respectively. The higher LA content caused the stronger movement of these peaks. This anomaly indicated the change in TGS crystalline structure in the presence of LA.

The LA impurity made changes in functional groups as well. The results are presented in Fig. 1 b. Obviously, LA led to the significant expansion of a broad band for TGS at 3300 – 2800 cm^{-1} which characterizes the presence of water molecules as well as the number of hydrogen bonds formed in crystals [9 – 11]. From our point of view, the second one related to the formation of new hydrogen bonds could be reasonable because the content of water molecules must be the same under identical synthesis conditions. Additionally, adsorption peaks of LA at 1512 and 915 cm^{-1} corresponding to NH^{3+} bending and C-H vibrations were also found in LA-Doped TGS samples (Fig. 1 b).

Reliability of the synthesized composite samples can also be confirmed by measuring the dependencies of dielectric constant on temperature as conducted in previous studies [8, 15, 16].



a



b

Fig. 1. Characterization of pure and LA-Doped TGS at different LA content. (a) XRD patterns and (b) FTIR spectra

In this study, the results are shown in Fig. 2 at different LA content and the observed phase transition points T_c are provided in Table 1.

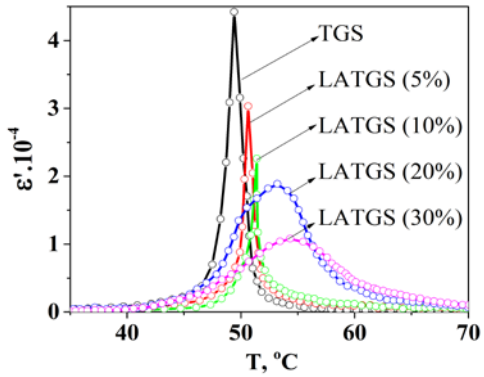


Fig. 2. Phase transition in TGS at different LA content

In the case of pure TGS, the Curie point T_c was detected at 49.2 °C i.e. slightly higher than the literature ones (T_c = 49 °C). This was not a surprise that under synthesis conditions of negative temperatures, additional polar groups of water could be formed in TGS crystals [8]. When

introducing LA intro TGS, the T_c shifted to higher temperatures. The results were in good agreement with the reported data published in several works and therefore confirmed the quality of LA containing TGS crystals. In this regard, the samples are ready for testing frequency spectra – the subject of this study.

It should be added that all the dielectric measurements in this study were carried out in b-direction of crystals. This is very important to compare the obtained results to verify the utilized research method.

Table 1. Phase transitions temperatures in TGS with different LA content

Samples	T_c, °C
Pure TGS	49.2
LATGS (5 %)	50.6
LATGS (10 %)	51.3
LATGS (20 %)	53.1
LATGS (30%)	54.2

3.2. Frequency spectra of dielectric loss

The frequency spectra of dielectric loss $\varepsilon''(f)$ for pure and LA-doped TGS are presented in Fig. 3 (Table 2) and Fig. 4 in dependence on temperature and LA content, respectively. Fig. 4 was replotted from Fig. 3 to demonstrate the influence of LA. Regarding the temperature effect (Fig. 3), the increase in annealing temperature (25 → 40 → 45 → 49 °C) led to the shift of $\varepsilon''(f)$ peaks toward higher frequencies i.e. the temperature dependences have the nature of activation processes. This tendency was observed frequencies (f_m) determined at $\varepsilon''(f)$ peaks at different temperatures are listed in Table 2. When adding LA into TGS, in the contrast to the above case of increase in T_c (Fig. 2), the higher LA content (0 → 5 → 10 → 20 → 30 wt.%) resulted in the reduction of relaxation frequencies (Fig. 4, Table 2). Notably, the presence of relaxation peaks found at the region of $10^5 – 10^7$ Hz for pure TGS (Fig. 3 a) is similar to that published in previous studies [9, 25]. The nature of the frequency peak movement as described above in relation to the shift of phase transition point will be discussed thoroughly in this study.

To more clearly represent the influence of LA, dependences of phase transition point (T_c) and relaxation frequencies (f_m) on LA content were plotted in Fig. 5.

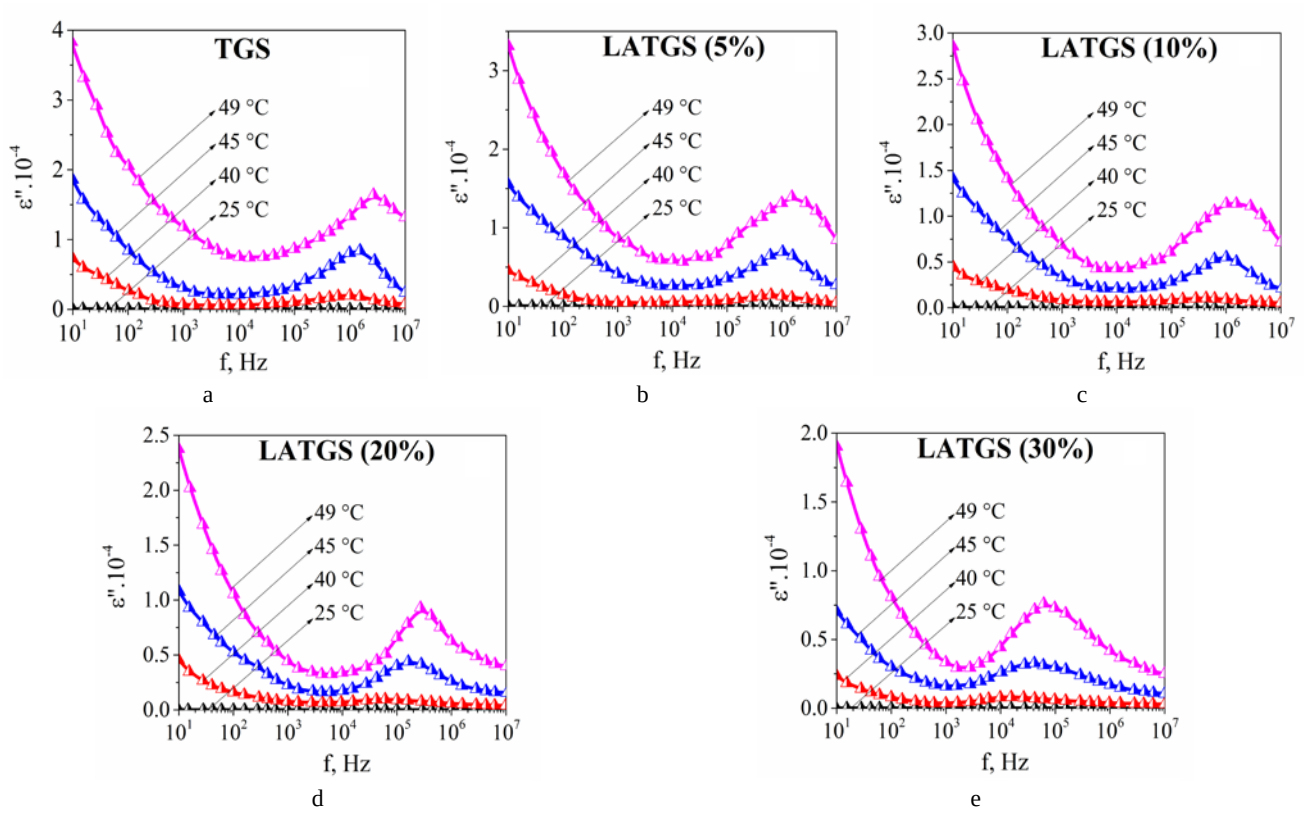


Fig. 3. Frequency spectra of dielectric loss in dependence on annealing temperature: a – for pure TGS; b – TGS doped with LA of 5%; c – with LA of 10%; d – with LA of 20%; e – with LA of 30%

Table 2. Relaxation frequencies exported from frequency spectra (Fig. 3 and Fig. 4) for TGS at different LA content and temperatures

Samples	f_m, MHz			
	25 °C	40 °C	45 °C	49 °C
Pure TGS	0.292	0.948	1.362	2.740
LATGS (5 %)	0.126	0.639	1.029	1.564
LATGS (10 %)	0.063	0.421	0.896	1.251
LATGS (20 %)	0.006	0.061	0.172	0.269
LATGS (30 %)	0.002	0.014	0.039	0.063

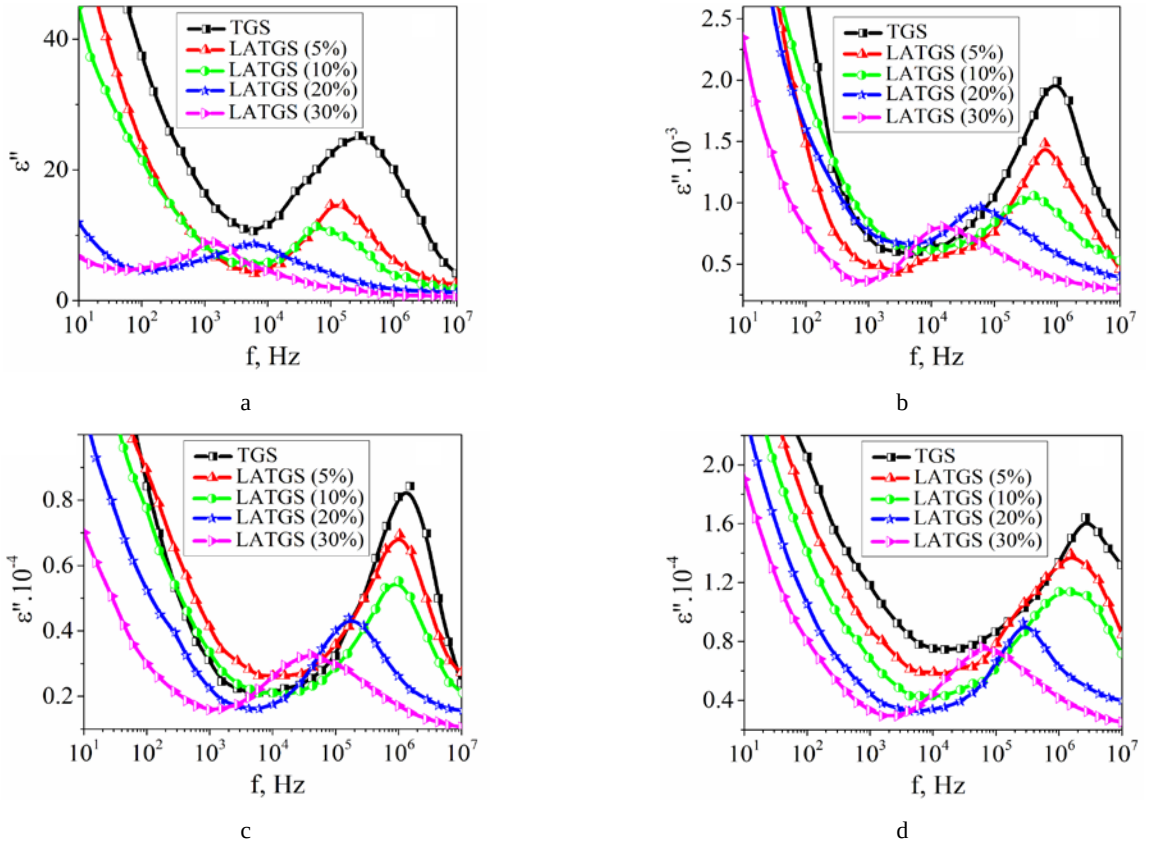


Fig. 4. Frequency spectra of dielectric loss in dependence on LA content at temperatures: a – 25 °C; b – 40 °C; c – 45 °C; d – 49 °C

The relaxation frequencies were shown at different annealing temperatures of 25, 40, 45 and 49 °C (Fig. 5). Obviously, with increasing LA content, the change of f_m and T_c occurred in opposite directions as described above. Thus, observing the movement of f_m with LA content allows us to predict the changing tendency of phase transition in LATGS. Moreover, this can also help to clarify the nature of the influence of LA on TGS properties that will be thoroughly discussed below in the present work.

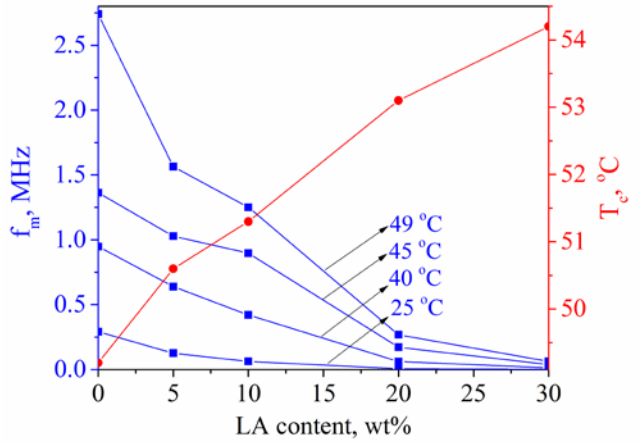


Fig. 5. Dependences of peak frequencies (f_m) at different temperatures and phase transition point (T_c) on LA content in TGS

Based on the values of relaxation frequencies, the relaxation time τ ($\tau = 1/2\pi f_m$) was calculated, and the obtained results were in good agreement with the Arrhenius law [26]:

$$\tau = Ae^{\frac{\Delta E}{kT}}, \quad (1)$$

where A is a constant, ΔE is the activation energy, k is the Boltzmann constant and T is the temperature in Kelvin. The fitting of experimental data with Arrhenius law is expressed in dependences of Lnτ versus the inverse temperature ($1/T$) in the form of straight lines as shown in Fig. 6.

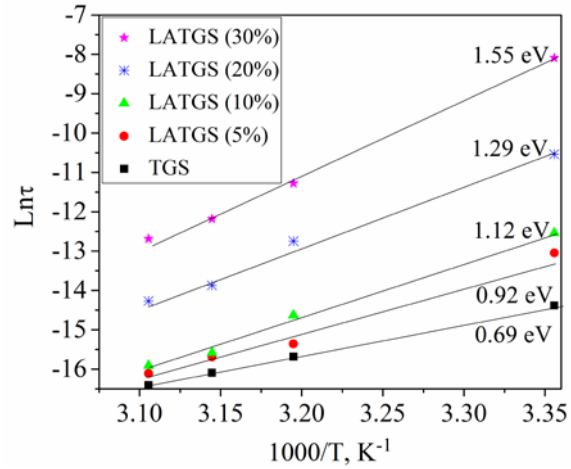


Fig. 6. Dependences of relaxation time on temperature for TGS at different LA content

According to Eq. 1, the activation energies for TGS containing different LA content were also determined. The

presence of LA in TGS structure led to the rise of activation energies (0.69 (TGS) → 0.92 (LATGS5%) → 1.12 (LATGS10%) → 1.29 (LATGS20%) → 1.55 eV (LATGS 20 %)) (Fig. 6). It is important to emphasize that the values of ΔE = 0.69 *eV* for pure TGS is slightly greater than that published in several works [25, 27], probably, due to the polar defects appeared during the crystal growth at negative temperatures [8], which maintain the polar state and drag the phase transition point of TGS to higher temperatures (T_c = 49.2 °C) (Fig. 2). Known that the activation energy (ΔE = 0.69 *eV*) of TGS is directly related to the nature of hydrogen – bond systems in TGS, and therefore the influence on which will affect phase transition characteristics in TGS. As mentioned above, the presence of LA in TGS led to the change in ΔE, or LA obviously intervened the hydrogen bond structure of TGS.

3.3. Discussion

What do we see from the presented frequency spectra of $\varepsilon''(f)$ in relation to the increase in phase transition temperature of LATGS? First of all, it is needed to find out the theoretical basis of this idea. Known [28] that TGS has 180° domain wall (DW) structure and its motion under the application of an external periodic electric field *E* can be described by the following equation:

$$kX + \eta \ddot{X} = 2P_s E \ , \qquad (2)$$

where *k*, η characterize for the elasticity and viscosity in the sample medium, respectively; *X* is the displacement, and P_s is the spontaneous polarization. From Eq. 2, the relaxation frequencies f_m can be estimated as follows:

$$f_m = \frac{1}{\eta D} \ , \qquad (3)$$

where *D* is the average domain width. In this regard, the influence of the viscosity η plays a crucial role in the change of relaxation frequencies because the domain became more stable and is not changed much in the presence of LA [18], and therefore *D* could not be the main cause for the detected strong shift of relaxation frequencies. Indeed, as seen in Fig. 6, the activation energies characteristic for the DW motion in TGS increased. It means that DWs were more difficult to move when LA content increased, and this anomaly was related to their interaction with LA through hydrogen bonds. This interaction will stabilize the polar state of the ferroelectric phase and therefore the LATGS structure can be transformed into a symmetric (paraelectric) phase only at higher temperatures i.e. the phase transition point will shift toward higher – temperature region as shown in Fig. 2. On the other hand, as demonstrated in Fig. 3 and Fig. 4, the LA dragged f_m toward lower frequencies or the addition of LA into TGS resulted in the increase in the viscosity according to Eq. 3. Thus, the viscosity created by LA/TGS interaction led to the decrease in relaxation frequencies and to the increase in phase transition temperature at the same time. In this regard, by observing the shift direction of relaxation frequencies f_m we can predict the phase transition tendency of LA-doped TGS, as well as explain the nature of these anomalies based on the terminology of hydrogen bonds and DW motion.

According to the above discussion, the decrease in relaxation frequencies with increasing LA content might be understood due to the stronger interaction of LA with TGS leading to the increased viscosity in samples. This assumption is confirmed by the expansion of 3500 – 2900 cm^{-1} absorption band shown in FTIR spectra (Fig. 1 b) with increasing LA content.

It is worth noting that the presence of hydrogen bonds between LA and TGS resulted in the increase in bias electric field in samples, leading to the shift of phase transition.

4. CONCLUSIONS

The analysis of frequency spectra of dielectric loss has successfully clarified the well-known increase in phase transition temperature in L,α-alanine doped TGS. By using the frequency spectra of dielectric loss, the nature of phase transition in LATGS has been figured out. With increasing LA content, the shift of phase transition and relaxation frequency positions occurred in opposite directions. The increase in phase transition temperature was accompanied by a decrease in relaxation frequencies. Based on the frequency spectra, the reason was found to be related to the enhanced viscosity created by the strong interaction between L,α-alanine and TGS structure through hydrogen bonds, which inhibited the domain wall motion in TGS. Thus, the frequency spectra are useful to evaluate the effect of LA amino acids on TGS properties as well as clarifying the nature of this influence. The study is useful to expand the current application scope of TGS related materials.

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